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# Durability of Thin PECVD SiO<sub>x</sub> Coatings on Polymer Films

Y. Leterrier and J.-A. E. Månson, Laboratoire de Technologie des Composites et Polymères,  
Ecole Polytechnique Fédérale de Lausanne, Switzerland;  
and G. Rochat and P. Fayet, Tetra Pak (Suisse) SA, Tetra Pak Materials R&D, Switzerland

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## ABSTRACT

The durability of plasma enhanced chemical vapor deposited SiO<sub>x</sub> coatings on polyethylene and polyethylene terephthalate films is presented with attention paid to the oxide cohesive and adhesive strengths. A micromechanical modeling of the fragmentation behavior of the coating upon uniaxial straining of the coated polymer is derived. SiO<sub>x</sub> crack onset strain of the order of 5% and tensile strength as high as 4 GPa are measured and found independent of the nature of the polymer substrate. The interface shear strength is found to be equal to 170 MPa in the case of PET/SiO<sub>x</sub>, and to 107 MPa in the case of LDPE/SiO<sub>x</sub>. These results are discussed in light of the mechanical behavior and the surface properties of the polymer substrates.

## INTRODUCTION

Recent progress in the development of plasma assisted deposition techniques on polymer films has led to the development of novel oxygen barrier materials, of central interest for food and pharmaceutical packaging industries [1]. During manufacture and service of the package, the limiting factor is the durability of the barrier layer, which should not crack or detach from the substrate. Cracks are controlled by the cohesion of the oxide coating, whereas delamination is controlled by the adhesion of the coating to the polymer. Numerous methods and models have been developed in the past decades to determine these two parameters [2]. Adhesion test methods either introduce a third body to solicit the interface, or use model specimens to apply thermal or mechanical loads to the interface without the need for a third body. The former, developed mainly to assess coating adhesion, include the tape and similar pull-off methods, and the scratch and indentation tests, which do not necessarily reflect the buried character of the interface. Alternatively, the fragmentation test was developed as a reliable technique to investigate coating durability, as it simulates the typical stress conditions achieved during manufacture and service. This approach has already proven its relevance to analyze the effect of temperature, annealing, oxide thickness and stoichiometry on coating durability in case of alternative barrier films [3, 4]. The work is devoted to the case of plasma enhanced chemical vapor deposited (PECVD) SiO<sub>x</sub> coatings on polyethylene terephthalate (PET) and low density poly-

ethylene (LDPE) films, with the aim to relate the durability of the oxide coating to the mechanical and surface properties of both polymers.

## MICROMECHANICAL ANALYSIS OF THE STRESS TRANSFER AT THE POLYMER-OXIDE INTERFACE

The interface shear strength,  $\tau$ , was derived from the classical Kelly-Tyson model of stress transfer [5], adapted to the thin film geometry:

$$\tau = 1.337 \cdot h \cdot \frac{\sigma_{\max}(l_c)}{\bar{l}_{\text{sat}}} \quad (1)$$

where  $h$  is the coating thickness,  $\sigma_{\max}$  is the coating strength at critical length  $l_c$ , and  $\bar{l}_{\text{sat}}$  is the average fragment size at saturation directly measured from micrographies of fragmented specimens above the saturation onset strain, to be detailed later. The critical length  $l_c$  was calculated to be very close to  $3/2 \cdot \bar{l}_{\text{sat}}$  [6] providing that no delamination is present at saturation. The dependence of the oxide strength  $\sigma_{\max}$  with fragment length was calculated from a linear extrapolation of the initial part of the curve  $\ln\{\text{CD}\}$  vs.  $\ln\{\epsilon\}$ , where CD is the crack density and  $\epsilon$  is the nominal strain, assuming a two-parameter ( $\alpha$  and  $\beta$ ) Weibull distribution [7, 8]:

$$\sigma_{\max}(l) = \beta \cdot (l/l_0)^{-1/\alpha} \cdot \Gamma\{1 + 1/\alpha\} \quad (2)$$

where the normalizing factor  $l_0 = 1 \mu\text{m}$  and  $\Gamma$  is the gamma function. Of central interest is also the crack onset strain  $\epsilon_f$ , which depends strongly upon coating thickness. It was modeled following a linear elastic fracture mechanics (LEFM) approach related to the energy released by crack growth [4]:

$$\epsilon_f = \frac{C}{\sqrt{h_c(h_s + h_c)}} \quad (3)$$

Where  $h_s$  and  $h_c$  are the coating and substrate thickness, and  $C$  is a shear lag parameter equal to  $1.7 \cdot 10^{-8} \text{ m}$ , determined from the crack onset strain found equal to 1.4% for a 120 nm thick SiO<sub>x</sub> coating on PET. In the present case, the crack

onset strain of the 20 nm thick coating is predicted from Equation 3 to be 3.4%.

## EXPERIMENTAL

The materials investigated were 12  $\mu\text{m}$  thick PET and 40  $\mu\text{m}$  thick LDPE biaxially stretched films, coated with a  $20\pm 3$  nm thick  $\text{SiO}_x$  layer, where the stoichiometry ratio  $x$  was in the range 1.8 to 2. The coating deposition was done using plasma enhanced chemical vapor deposition (PECVD). In the deposition process, the polymer substrate was mounted in the deposition chamber under 0.1 mbar. The silane source was hexamethyl-disiloxane, pumped into the chamber together with oxygen and argon. The Young's modulus of the oxide coating was assumed to be equal to 79.5 GPa [6]. In the fragmentation test, coated samples were loaded in tension and the resulting fragmentation of the coating was recorded as a function of applied strain. The fragmentation tests were performed at room temperature on a Minimat Miniature Materials Tester (Rheometrics) at a constant strain rate of  $4.2 \cdot 10^{-4} \text{ s}^{-1}$  for the PET and  $3.5 \cdot 10^{-4} \text{ s}^{-1}$  for the LDPE. Strained specimens were kept under strain with special fixtures and loaded into a scanning electron microscope chamber for morphological analyses.

## RESULTS AND DISCUSSION

Figure 1 shows the fragmentation process of the oxide coating on the PET substrate. The onset of cracking was detected at 5% strain, by far higher than the value of 1.4% measured on the 120 nm thick coating. It is also higher than the predicted value of 3.4%, which would indicate that the oxide toughness, included in the shear lag parameter  $C$  of Equation 3, is higher for thinner coatings. Interestingly, cracks initiate on defects zones, propagate first along one direction and then across the whole specimen width forming well defined fragment strips. A fast increase in crack density is observed, and, around 15% strain, dark features parallel to the applied stress develop within individual strips. These features are tent-shaped buckling failures of the coating, resulting from Poisson ratio effects. Further cracking occurs at higher strains, and, around 25% strain, the crack density becomes constant and equal to ca  $1.6 \mu\text{m}^{-1}$ , defining the saturation regime. The fragmentation sequence of the oxide coating on the LDPE substrate is presented in Figure 2. Similarly to the PET case, the crack onset strain was found to be close to 5%. However, the fragmentation increase is slower, and the saturation regime is reached around 50% strain, with a crack density close to  $1.1 \mu\text{m}^{-1}$ .

It is important to stress at this point that a strain recovery of the order of 3% has been measured upon unloading strained PET specimens [3]. As a consequence, although cracks are formed beyond 5% strain, the barrier performance will only deteriorate significantly for films strained beyond 8% strain. A higher effect is even expected in the case of LDPE due to higher strain at yield.

These observations are synthesized in Figure 3 in the form of CD vs. strain plots. The fragmentation process of 120 nm thick coatings on PET is also shown. The cohesive strength  $\sigma_{\text{max}}$  derived from the initial stage of the fragmentation process is calculated to be  $4\pm 0.8$  GPa for both 20 nm thick coatings, whereas it is  $1.5\pm 0.3$  GPa for the 120 nm thick coating. The reason for such high strength for the 20 nm thick coating is related to the fact that only volume defects contribute to the strength variation with coating thickness. Therefore thinner coatings are expected to have higher strength. This was clearly observed in the case of evaporated oxides [4]. The interfacial strength between the oxide and PET is found to be equal to 170 MPa, and to 107 MPa in the case of LDPE. These values should be compared to the bulk shear stress of the polymer, and are largely a result of the strain hardening behavior of the polymer under the high plastic stress developed during the fragmentation test [3].

The high adhesion levels and small amount of delamination result from the chemical interactions between the polymer and  $\text{SiO}_x$  obtained by PECVD. In the case of PET, these interactions involve C-Si and C-O-Si chemical bonds [9, 10] and most likely hydrogen interactions established between silanols groups of the oxide and the carboxylic functions of the polymer, whose acid-base character are known to increase considerably the work of adhesion between basic-type polymers and silicon oxide [11]. In case of LDPE it is likely that the good adhesion results from surface activation of the polymer achieved during the plasma process, which indeed has been shown to be a prerequisite to achieve a good barrier [9], as it would to overcome the polymer surface roughness. Work is in progress to relate the adhesion performance to the barrier properties of the LDPE film.

## CONCLUSIONS

The cohesive strength and adhesion of plasma enhanced chemical vapor deposited  $\text{SiO}_x$  coatings to polyethylene and polyethylene terephthalate films, of considerable interest for food packaging, were investigated as they both control the durability of the coating. These parameters were derived from a micromechanical modeling of the fragmentation behavior of the oxide coating upon uniaxial straining of the coated polymer. The experimental results and their analysis lead to several remarks.

- A simplified linear elastic fracture mechanics approach predicts a crack onset strain of the oxide of 3.4%, irrespective of the nature of the polymer substrate; the prediction provides a correct trend, although it underestimates the crack onset strain close to 5% directly observed under microscope.

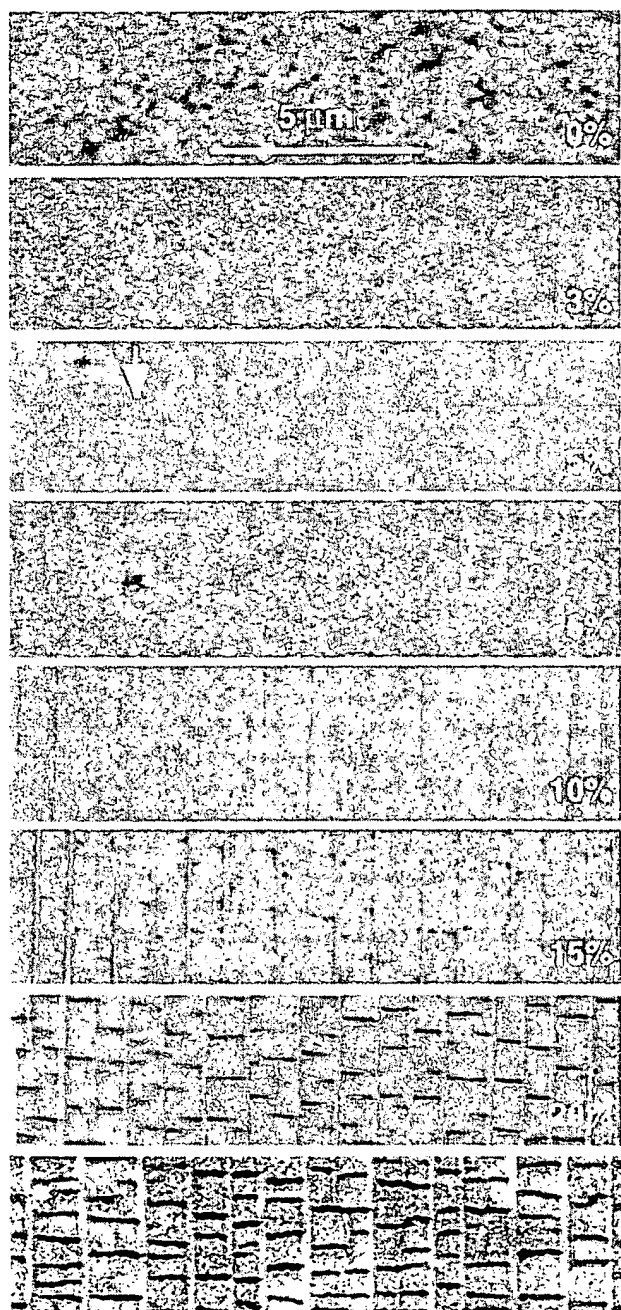


Figure 1. Fragmentation process of a 20 nm thick  $\text{SiO}_x$  coating during uniaxial straining of a  $12\ \mu\text{m}$  thick PET substrate. The applied strain is indicated in each micrograph. The arrow at 5% strain indicates the first observed crack.

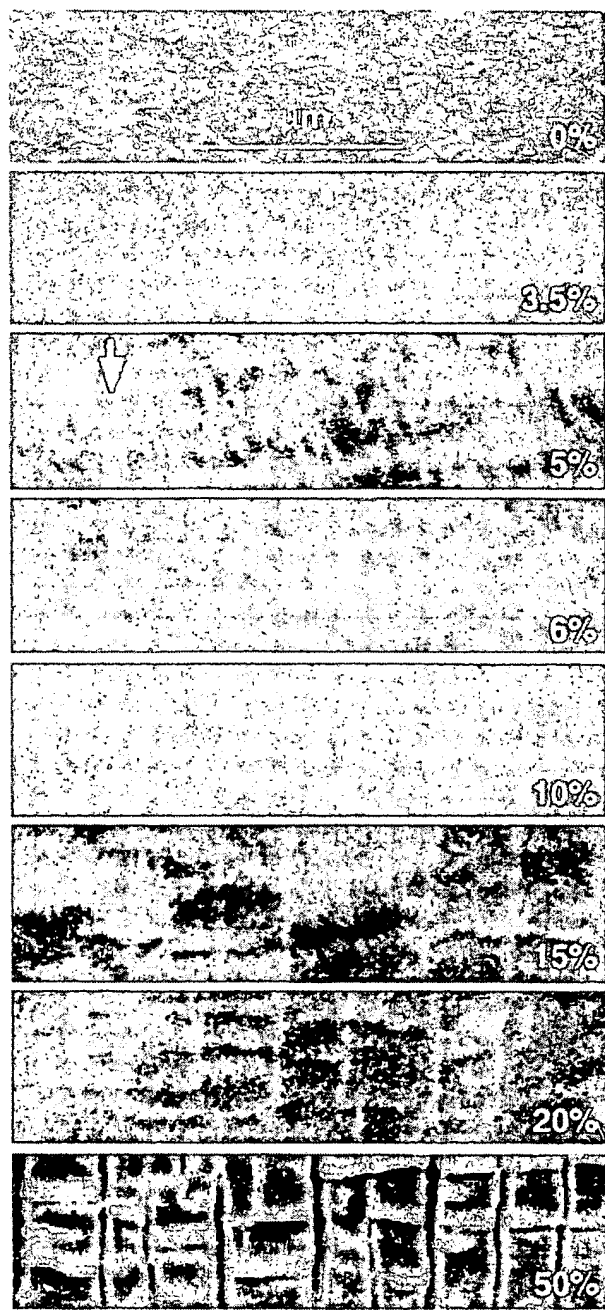


Figure 2. Fragmentation process of a 20 nm thick  $\text{SiO}_x$  coating during uniaxial straining of a  $40\ \mu\text{m}$  thick LDPE substrate. The applied strain is indicated in each micrograph. The arrow at 5% strain indicates the first observed crack.

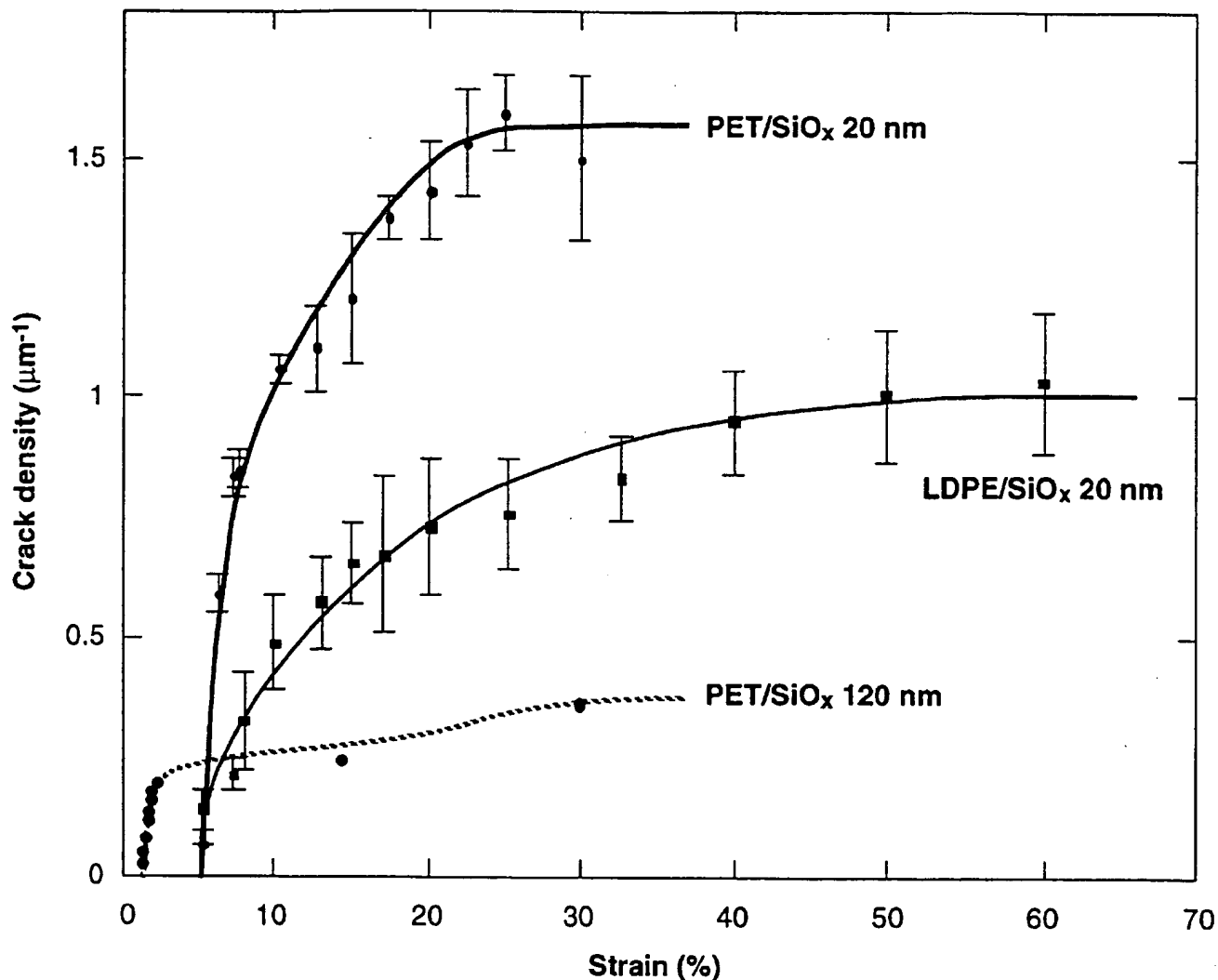


Figure 3. Crack density of the oxide coating vs. applied strain of PET and LDPE substrates.

- The tensile strength of the 20 nm thick SiO<sub>x</sub> coating is found to be as high as 4 GPa, in agreement with the fact that volume defects control the cohesion of the oxide, i.e., thinner coatings possess a higher strength.
- The interface shear strength between PECVD SiO<sub>x</sub> and PET or LDPE is as high as the bulk shear stress of the

polymers, as a result of their strain hardening capability. Such high adhesion levels further reflect the presence of chemical bonds at the interface and, most likely in the case of LDPE, that a surface activation of the polymer occurs during the deposition process.

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